# Relation between inelastic electron tunneling and vibrational excitation of single adsorbates on metal surfaces

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We analyse theoretically a relation between the vibrational generation rate of a single adsorbate by tunneling electrons and the inelastic tunneling (IET) current in scanning tunneling microscope, and the influence of the vibrational excitations on the rate of adsorbate motions. Special attention is paid to the effects of finite lifetime of the vibrational excitations. We show that in the vicinity and below the IET threshold the rate of adsorbate motion deviates from a simple power-law dependence on the bias voltage due to the effects of bath temperature and adsorbate vibrational lifetime broadenings. The temperature broadening appears to be confined near the threshold voltage within a narrow region of several  $k_BT$ , whereas the lifetime broadening manifests itself in a much wider region of applied voltages below the IET threshold.

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### I. INTRODUCTION

Since a pioneering demonstration of a single atomic switch by Eigler et~al., <sup>1</sup> in which high and low current state are realized via controlling Xe atom transfer between a Ni substrate and a tip of scanning tunneling microscope (STM), there have been very exciting developments in the unique ability of STM to induce the motions and reactions of single adsorbates at surfaces. Examples of such novel experiments are dissociation of decaborane on Si(111), <sup>2</sup> desorption of hydrogen from hydrogenterminated Si(100), <sup>3</sup> a step-by-step control of chemical reaction to form a biphenyl molecule from a iodobenzene on Cu(111), <sup>4</sup> rotation and dissociation of an oxygen molecule on Pt(111), <sup>5</sup> rotation of acetylene molecule on Cu (100), <sup>6</sup> hopping of CO on Pd(110), <sup>7</sup> and hopping and desorption of ammonia on Cu(100).

The theoretical understanding of the physical mechanisms behind these motions and reactions of single adsorbates has made a slow but steady progress toward a full understanding of how tunneling electrons couple to nuclear motion of an adsorbate to overcome the potential barrier along the relevant reaction coordinate. The power-law dependence of the atom transfer rate as a function of applied voltage or tunneling current observed for the Eigler switch has been modelled as a potential barrier crossing between the potential wells formed by the interaction of the the adatom with the tip and the substrate, respectively. The atom overcomes the potential barrier through the stepwise vibrational ladder climbing by inelastic tunneling electrons. The so-called vibrational heating due to inelastic tunneling electrons has been proposed by Gao et al.,9 Walkup et al.,10 and Brandbyge & Hedegard<sup>11</sup> [see also a detailed discussion in Ref. 12]. Arrhenius-like expression for the rate of motion is characterized by an effective temperature  $T_{\text{eff}}$  in the presence of inelastic tunneling current, otherwise a vibrational mode is in thermal equilibrium with a substrate temperature T.

Another possibility of coherent multistep vibrational excitation by a single electron has been proposed by Salam et al., 13 in analogy to a mechanism of desorption induced by electronic transition developed by Gadzuk.<sup>14</sup> The coherent multiple excitation mechanism was shown to be important at low tunneling currents, where the average time between successive electrons is longer than the vibrational lifetime. Dissociation rate of single O<sub>2</sub> on Pt(111), where the vibrational relaxation rate of the O-O stretch mode due to electron-hole pair excitations in the substrate is much larger than the tunneling current, <sup>15</sup> has been satisfactory described by this coherent multiple excitation process.<sup>5</sup> However, one should bear in mind that since both coherent and incoherent multiple excitation mechanisms show a power-law dependence over a limited range of the bias voltage or the tunneling current, they can not be simply distinguished.

Recently we have developed<sup>16,17,18</sup> a theory of vibrational tunneling spectroscopy of adsorbates on metal surfaces using the Keldysh-Green's function method<sup>19,20</sup> for an adsorbate-induced resonance model proposed by Persson and Baratoff.<sup>21</sup> This has enabled us to elucidate the elementary processes of electron transport via adsorbate state, and to obtain general formulae for the elastic and inelastic electron tunneling (IET), and the effective vibrational distribution function within the second-order perturbation over the electron-phonon interaction of adsorbates. In comparison with the earlier papers,<sup>9,11</sup> where the Keldysh formalism was used as well, we take into account self-consistently the effects of the finite vibration lifetime on the IET spectra as well as on the vibration generation rate.

In this work a relation between the IET current and vibrational generation rate is studied using the coupled Dyson and kinetic equations for causal and statistical phonon Keldysh-Green's functions. The stationary nonequilibrium phonon distribution function characterized by the current-driven vibrational generation rate and the vibrational relaxation rate allows us to introduce the effective temperature and to describe self-consistently the

IET-induced vibrational heating. A primary interest is focused on the vicinity and below the threshold of the vibrational excitation. This situation was not investigated in Refs. 9,10,11,12, where the limit of large applied voltage was considered,  $eV\gg\Omega$  ( $\Omega$  is the vibrational mode energy). As we show, the dependencies of the vibrational generation rate and of the multi-step adsorbate excitation rates on the bias voltage deviate from simple power laws due to the effects of bath temperature and a finite lifetime of the vibrational mode excited by tunneling electrons. Whereas the bath temperature broadening is restricted to a narrow region within several  $k_BT$ , the vibrational lifetime broadening causes a strong overheating effect in a much wider bias voltage region below the IET threshold.

The paper is organized as follows. In Section II the general formulation of the problem in terms of Keldysh-Green's functions is outlined, and the kinetic equation for vibrational excitation is derived. In Section III we analyze the expressions for the IET vibrational generation rates and IET current. The physical meaning of IET vibrational generation rate is discussed in Subsection III A. In subsection III B the limiting cases of low bath temperature and no vibrational broadening are analyzed, and it is shown that in this limit our results coincide with those received previously in Refs. 9,10,11,12. Numerical examples are discussed in Subsection III C.

# II. THEORY

We consider the same Hamiltonian as used before  $^{12,16,17,18,21}$ 

$$\mathcal{H} = \sum_{k} \varepsilon_{k} c_{k}^{\dagger} c_{k} + \sum_{p} \varepsilon_{p} c_{p}^{\dagger} c_{p} + \varepsilon_{a} c_{a}^{\dagger} c_{a} + \Omega(b^{\dagger} b + 1/2)$$

$$+ \sum_{k} \left( V_{ka} c_{k}^{\dagger} c_{a} + \text{h.c.} \right) + \sum_{p} \left( V_{pa} c_{p}^{\dagger} c_{a} + \text{h.c.} \right)$$

$$+ \chi c_{a}^{\dagger} c_{a} (b^{\dagger} + b), \tag{1}$$

where the energies and annihilation operators of a substrate, a tip, an adsorbate orbital and a vibrational mode are denoted by  $\varepsilon_p, \varepsilon_k, \varepsilon_a, \Omega$  and  $c_p, c_k, c_a, b$ , respectively. The tip and substrate systems are assumed to be in thermal equilibrium at the same temperature T, and to have independent chemical potentials  $\mu_t$  and  $\mu_s$ , respectively, whose difference corresponds to the bias voltage  $eV = \mu_s - \mu_t$ . Electronic tunneling matrix elements  $V_{ka}$  (tip-adsorbate) and  $V_{pa}$  (substrate-adsorbate) give rise to stationary current between the tip and the substrate through the adsorbate orbital. The distribution function for electrons of the tip and substrate systems,  $n_t$  and  $n_s$  respectively, are given by the Fermi distribution function.  $\chi$  is the vibration-adsorbate orbital coupling constant.

In the Keldysh-Green's function method<sup>19</sup> the nonequilibrium process of the electron tunneling between the tip and substrate through the adsorbate level

is described by the *coupled* Dyson and kinetic equations for causal and statistical Keldysh-Green's functions. This *coupled* description of the dynamical and statistical properties of the nonequilibrium system allows, within the Keldysh-Green's function method, to find *self-consistently* the spectra *and* occupation numbers changes which are introduced into the system by the external action (the tip-substrate bias voltage in our case), mediated by the interactions in the system. In what follows, the implementation of the the Keldysh-Green's function method for the Hamiltonian (1) is outlined by Eqs. (2)-(10) without detailed explanations; the latter can be found in the original paper by Keldysh<sup>19</sup>, see also in Refs. 20, 16,17,18.

The kinetic equation for vibrational excitations (phonons) takes the form

$$\frac{\partial N_{\rm ph}}{\partial t} = \int \frac{d\omega}{2\pi} \left[ \Pi^{+-}(\omega) D^{-+}(\omega) - \Pi^{-+}(\omega) D^{+-}(\omega) \right]. \tag{2}$$

Here the phonon Keldysh-Green's functions  $D^{\pm\mp}$  are given by

$$D^{+-}(\omega) = n_{\rm ph}(\omega)[D^r(\omega) - D^a(\omega)]$$

$$= -2i\pi n_{\rm ph}(\omega)\rho_{\rm ph}(\omega),$$
(4)

$$D^{-+}(\omega) = [1 + n_{\rm ph}(\omega)][D^r(\omega) - D^a(\omega)]$$
  
=  $-2i\pi[1 + n_{\rm ph}(\omega)]\rho_{\rm ph}(\omega),$ 

where  $n_{\rm ph}(\omega)$  is the vibration occupation function to be determined self-consistently from the kinetic equation, and the phonon retarded and advanced Green's functions are given by

$$D^{r}(\omega) = \frac{1}{\omega - \Omega + i\gamma_{eh}(\omega)/2},$$

$$D^{a}(\omega) = \frac{1}{\omega - \Omega - i\gamma_{eh}(\omega)/2}.$$
(5)

Here  $\gamma_{eh}(\omega) = -2 \operatorname{Im} \Pi^r$  (where  $\Pi^r$  is the retarded phonon polarization operator) is the vibrational damping rate due to electron-hole pair excitations in the substrate and tip.<sup>22</sup> We omit here the real part of  $\Pi^r$ , which gives a red shift of the resonant frequency  $\Omega$ .

The phonon polarization operators  $\Pi^{\pm\mp}$  and  $\Pi^r$  are calculated in the second order perturbation over  $\chi$ . For example,

$$\Pi^{+-} = i\chi^2 \int \frac{d\varepsilon}{2\pi} G_a^{+-}(\varepsilon + \omega) G_a^{-+}(\varepsilon), \tag{6}$$

$$\Pi^{r} = i \frac{\chi^{2}}{2} \int \frac{d\varepsilon}{2\pi} \left[ G_{a}^{a}(\varepsilon) F_{a}(\varepsilon + \omega) + F_{a}(\varepsilon) G_{a}^{r}(\varepsilon + \omega) \right], \tag{7}$$

where the retarded, advanced and statistical Keldysh-Green's functions of the adsorbate are connected as

$$F_{a}(\varepsilon) = [1 - 2n_{a}(\varepsilon)][G_{a}^{r}(\varepsilon) - G_{a}^{a}(\varepsilon)]$$

$$= -2i\pi[1 - 2n_{a}(\varepsilon)]\rho_{a}(\varepsilon),$$
(8)

with the adsorbate density of states  $\rho_a$  and occupation function  $n_a$ ,

$$\rho_a(\varepsilon) = (1/\pi)\Delta/[(\varepsilon - \varepsilon_a)^2 + \Delta^2], \tag{9}$$

$$n_a(\varepsilon) = \frac{n_s(\varepsilon)\Delta_s + n_t(\varepsilon)\Delta_t}{\Delta}.$$
 (10)

Here  $\Delta = \Delta_t + \Delta_s$  is the resonant width of the adsorbate orbital,  $\Delta_{t(s)}(\varepsilon) = \pi \sum_{k(p)} |V_{k(p)a}|^2 \delta(\varepsilon - \varepsilon_k)$  is the

partial width due to the hybridizations between the tip and the adsorbate (substrate and adsorbate). The corrections (due to the vibration-adsorbate interaction) to the adsorbate density of states and to the adsorbate occupation function, Eqs.(9) and (10), respectively, are in the second order over the coupling constant  $\chi$ . Thus, they can be neglected in Eqs.(6,7) which are already written in the second order over  $\chi$ .

Then Eq. (2) leads to

$$\frac{\partial N_{\rm ph}}{\partial t} = 2\pi \chi^2 \int d\varepsilon d\omega \rho_a(\varepsilon) \rho_a(\varepsilon + \omega) \rho_{\rm ph}(\omega) \left[1 - n_a(\varepsilon)\right] n_a(\varepsilon + \omega) - \int d\omega \gamma_{eh}(\omega) n_{\rm ph}(\omega) \rho_{\rm ph}(\omega), \tag{11}$$

where  $\rho_{\rm ph}(\varepsilon) = (1/2\pi)\gamma_{eh}(\omega)/[(\omega-\Omega)^2 + \gamma_{eh}^2(\omega)/4]$  is the vibrational density of states with the broadening, and the vibrational damping rate (or linewidth)  $\gamma_{eh}$  due to electron-hole pair excitation is

$$\gamma_{eh}(\omega) = 2\pi\chi^2 \int d\varepsilon \left[ n_a(\varepsilon) - n_a(\varepsilon + \omega) \right] \rho_a(\varepsilon) \rho_a(\varepsilon + \omega) \approx 2\pi\chi^2 \frac{\Delta_s \rho_a^2(\mu_s) + \Delta_t \rho_a^2(\mu_t)}{\Delta} \omega. \tag{12}$$

The last approximate equation in (12) is valid in the limit of low-temperature,  $k_BT \ll \omega$  and slow-varying  $\rho_a(\varepsilon)$  over eV.

Adding and subtracting integral term  $\int d\omega \gamma_{eh}(\omega) n_T(\omega) \rho_{\rm ph}(\omega)$  to the kinetic equation (11), it

can be transferred to a more transparent form, showing that in the absence of the applied voltage the stationary phonon distribution function is the equilibrium one,  $n_T(\omega) = (e^{\omega/k_BT} - 1)^{-1}$ ,

$$0 = \frac{\partial N_{\rm ph}}{\partial t} = \int d\omega \rho_{\rm ph}(\omega) \left\{ \Gamma_{\rm in}(\omega) - \gamma_{eh}(\omega) \left[ n_{\rm ph}(\omega) - n_T(\omega) \right] \right\}. \tag{13}$$

Here

$$\Gamma_{\rm in}(\omega) = 2\pi \chi^2 \frac{\Delta_s \Delta_t}{\Delta^2} \int d\varepsilon \rho_a(\varepsilon) \rho_a(\varepsilon + \omega) \left[ n_s(\varepsilon + \omega) - n_t(\varepsilon + \omega) \right] \left[ n_s(\varepsilon) - n_t(\varepsilon) \right], \tag{14}$$

is the vibrational generation rate function.

# III. RATES OF VIBRATIONAL GENERATION AND ADSORBATE MOTION BY TUNNELING CURRENT

Kinetic equation Eq. (13) in the stationary regime allows us to find the stationary distribution function  $n_{\rm ph}(\omega)$  which deviates from the equilibrium one  $n_T(\omega)$ . The consequences of this deviation on the rate of adsorbate motion can be analysed within the truncated oscillator model, introduced and fully described in Ref. 12. The main quantities in the truncated oscillator model<sup>12</sup> are the the vibrational excitation and deexcitation rates between the nearest-neighboring levels of the harmonic oscillator,  $\Gamma_{\uparrow}$  and  $\Gamma_{\downarrow}$ , respectively. Knowing  $\Gamma_{\uparrow,\downarrow}$ , it be-

comes possible, as shown in Ref. 12, to introduce the adsorbate effective temperature

$$T_{\text{eff}} = \frac{\Omega}{k_B} \left( \ln \frac{\Gamma_{\downarrow}}{\Gamma_{\uparrow}} \right)^{-1}, \tag{15}$$

and, solving the oscillator master equation, to estimate the rate of adsorbate motion  ${\rm as}^{12}$ 

$$R(V) = n\Gamma_{\uparrow}(\frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}})^{n-1}, \tag{16}$$

where n is the number of the vibrational levels within the truncated harmonic approximation for the potential well, and  $(n-1)\Omega$  is assumed to be close to the barrier

height. Equation (16) can be also written<sup>12</sup> as Arrheniuslike expression via the effective temperature,

$$R(V) = n\Gamma_{\uparrow} \exp\left[-\frac{(n-1)\Omega}{k_B T_{\text{eff}}(\Omega)}\right]. \tag{17}$$

In what follows, we generalize the equations for the excitation and deexcitation rates from Ref. 12, in order to include the effect of the finite lifetime broadening of the vibrational excitations. The solution of the kinetic equation (13) for the stationary vibrational occupation number

$$N_{\rm ph} = \int d\omega \rho_{\rm ph}(\omega) n_{\rm ph}(\omega) \tag{18}$$

can be read as the  $\it effective$  Bose-Einstein distribution function

$$N_{\rm ph} = \left[\exp(\Omega/k_B T_{\rm eff}) - 1\right]^{-1}$$
 (19)

in the presence of the IET-driven generation  $\Gamma_{\rm iet}$  in competing to its damping  $\gamma$ . Comparing the latter with the definition of the effective temperature via the excitation and deexcitation rates, Eq. (15), and taking into account the explicit form of the kinetic equation (13), these rates can be written as

$$\Gamma_{\uparrow} = n_T(\Omega)\bar{\gamma}_{eh} + \Gamma_{\text{iet}}, \ \Gamma_{\downarrow} = [n_T(\Omega) + 1]\bar{\gamma}_{eh} + \Gamma_{\text{iet}}, \ (20)$$

where, in contrast to Ref. 12, the effect of the vibrational lifetime broadening is included into the generalized form of the IET vibration generation rate via the integration of  $\Gamma_{\rm in}$  over the lifetime-broadened vibrational density function,

$$\Gamma_{\rm iet} = \int d\omega \rho_{\rm ph}(\omega) \Gamma_{\rm in}(\omega),$$
 (21)

and

$$\bar{\gamma}_{eh} = \frac{\int d\omega \rho_{\rm ph}(\omega) \gamma_{eh}(\omega) n_T(\omega)}{n_T(\Omega)}$$
 (22)

is an averaged vibrational linewidth. Actually, because in reality the vibrational linewidth is always relatively small,  $\gamma_{eh} \ll \Omega$ , and  $\gamma_{eh}(\omega)$  is a slowly changing function at  $\omega \sim \Omega$ , a good approximation for Eq. (22) is  $\bar{\gamma}_{eh} \approx \gamma_{eh}(\Omega)$ .

We would like to note here that, in principle, we have to include additively (see the discussion above) the relaxation rates via other channels due to phonon excitations in the substrate  $\gamma_{\rm ph}$ , if they are important, and  $\gamma_{eh}$  is replaced by total relaxation rate,  $\gamma = \gamma_{eh} + \gamma_{\rm ph}$ .<sup>12</sup>

# A. Physical meaning of $\Gamma_{iet}$

Let us discuss the physical meaning of  $\Gamma_{iet}$  from the point of view of the elementary processes of the elastic

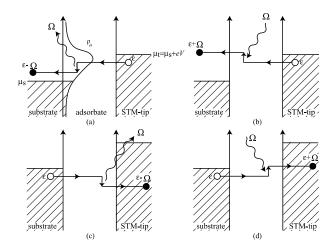


FIG. 1: Schematic representation of the inelastic electron transfers through the adsorbate from tip to substrate with emission and absorption of phonons  $R_{ts}^+$  and  $R_{ts}^-$ , (a) and (b), respectively. Same from substrate to tip with emission and absorption of phonons  $R_{st}^+$  and  $R_{st}^-$ , (c) and (d), respectively.

and inelastic electron tunneling through the adsorbate-induced resonance.

As has been noted in Ref. 17, the main difference between the elementary processes composing the inelastic current and the vibrational generation rate, is the fact that at  $T \neq 0$  there are inverse (hole) inelastic currents, which come with different signs to the total current and to the vibrational generation rate. The expression for the inelastic tunneling rate in the second order over  $\chi$ , [see Eqs. (14) from Ref. 17], can be written as

$$I_{\rm in}^{(2)}/e \equiv R_{\rm in}$$

$$= 2\pi \chi^2 \frac{\Delta_s \Delta_t}{\Delta^2} \int d\varepsilon \int d\omega \rho_a^{(0)}(\varepsilon) \rho_a^{(0)}(\varepsilon + \omega) \rho_{\rm ph}(\omega)$$

$$\times \{-n_s(\varepsilon + \omega) [1 - n_t(\varepsilon)] [1 + n_{\rm ph}(\omega)]$$

$$- n_s(\varepsilon) [1 - n_t(\varepsilon + \omega)] n_{\rm ph}(\omega)$$

$$+ [1 - n_s(\varepsilon)] n_t(\varepsilon + \omega) [1 + n_{\rm ph}(\omega)]$$

$$+ [1 - n_s(\varepsilon + \omega)] n_t(\varepsilon) n_{\rm ph}(\omega) \}.$$
(23)

As schematically illustrated in Fig. 1 each term of this equation has its own inelastic tunneling process, and it can be deconvoluted into

$$R_{\rm in} = +R_{st}^+ + R_{st}^- - R_{ts}^+ - R_{ts}^-. \tag{24}$$

Here  $R_{st}^{\pm}$  denotes the electron transfer rate through the adsorbate level with vibrational emission/absorption from substrate to tip (or a hole from tip to substrate), and  $R_{ts}^{\pm}$  is the reverse process from tip to substrate. In Figure 1, the initial electron states are shown as empty circles below the corresponding Fermi levels. The final states are shown as solid circles. In order that the partial currents  $R_{ij}^{\pm}$  are nonzero, the final states should be empty. For example, at T=0 and the applied voltage shown in Fig. 1, the currents shown in panels (c) and

(d) are zero. They become slightly nonzero at finite temperatures, due to thermal excitation of holes below the Fermi levels.

We turn now to the calculation of the vibrational generation rate. On the one side, it is zero in the stationary situation, Eq. (13). On the other side, it can be calculated within the same accuracy over  $\chi$  as Eq (24), summing up the electron transfer rates with vibrational generation and subtracting the rates with absorption, including the processes of generation and absorption leaving the electrons in substrate and in tip. The latter do not contribute into current and, thus, are absent in Eq (24). Then,

$$0 = R_{\rm ph}^{st} + R_{\rm ph}^{ss} + R_{\rm ph}^{tt}, \tag{25}$$

where, e.g.,

$$R_{\rm ph}^{st} = R_{st}^{(+)} - R_{st}^{(-)} + R_{ts}^{(+)} - R_{ts}^{(-)}, \tag{26}$$

compare the signs here with that in Eq. (24). After some algebra we obtain,

$$R_{\rm ph}^{st} \equiv R_{\rm ph}^{st} \{n_{\rm ph}(\omega)\}$$

$$= 2\pi \chi^2 \frac{\Delta_s \Delta_t}{\Delta^2} \int d\varepsilon \int d\omega \rho_a^{(0)}(\varepsilon) \rho_a^{(0)}(\varepsilon + \omega) \rho_{\rm ph}(\omega)$$

$$\times (n_s(\varepsilon + \omega) [1 - n_t(\varepsilon)] + n_t(\varepsilon + \omega) [1 - n_s(\varepsilon)]$$

$$+ n_{\rm ph}(\omega) [n_s(\varepsilon + \omega) + n_t(\varepsilon + \omega) - n_s(\varepsilon) - n_t(\varepsilon)].$$
(27)

It appears that, in order to calculate  $\Gamma_{\rm iet}$ , Eq.(21), via  $R_{\rm ph}^{st}$ , we have to replace in Eq. (28) the stationary nonequilibrium distribution function  $n_{\rm ph}(\omega)$  by the equilibrium one. Using notation of Eq. (27), it can be written as

$$\Gamma_{\rm iet} = R_{\rm ph}^{st} \{ n_T(\omega) \}. \tag{29}$$

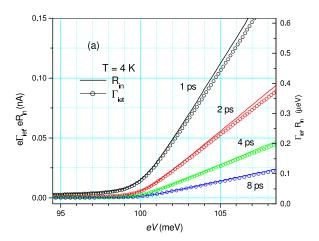
This means that there is a small but systematic difference between  $\Gamma_{\rm iet}$  Eqs. (29,26) and absolute value of IET rate  $|R_{\rm in}|$  Eqs. (23,24), growing with the increase of deviation of stationary vibration population  $n_{\rm ph}$  from the equilibrium one  $n_T$ , see also Eq. (32) below.

# B. Limit of T = 0 and no vibrational broadening

Before presenting the results of numerical calculation of  $\Gamma_{\rm iet}$ ,  $R_{\rm in}$ , and R at finite temperatures and including the effect of vibrational broadening, it is helpful to analyze the situation in the limit  $|eV| \gg \Omega \gg k_B T$ , neglecting the vibrational broadening,  $\rho_{\rm ph}(\omega) = \delta(\omega - \Omega)$ . For simplicity, we will also assume  $\Delta_s \gg \Delta_t$ . We expect to obtain the results equivalent to those in Gao et  $al.^{12}$ 

Equation (18) then reduces to

$$N_{\rm ph} = n_{\rm ph}(\Omega) = n_T(\Omega) + \frac{\Gamma_{\rm iet}}{\gamma_{eh}(\Omega)},$$
 (30)



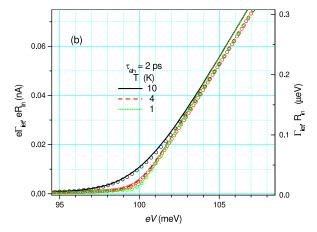


FIG. 2: Voltage dependences of the inelastic current  $R_{\rm in}$  and vibrational generation rate  $\Gamma_{\rm iet}$  (lines and lines with circles, respectively), calculated for T=4 K and different vibrational lifetimes (a); for  $\tau_{eh}=2$  ps and different temperatures (b). The vibrational frequency is taken  $\Omega=100$  meV. See other parameters in the text.

with

$$\Gamma_{\text{iet}} = \Gamma_{\text{in}}(\Omega) = 2\pi \chi^2 \frac{\Delta_s \Delta_t}{\Delta^2} \rho_a(\mu_t) \rho_a(\mu_t - \eta \Omega) \frac{F(x)}{\Omega}$$

$$\simeq \frac{\Delta_t}{\Delta_s} \gamma_{eh}(\Omega) \frac{F(x)}{\Omega}, \tag{31}$$

where  $F(x) = x\theta(x)$ ,  $x = |eV| - \Omega$ , and  $\eta = \text{sign}(V)$  is the sign function and  $\theta$  is the step function. In the last step we have used  $\rho_a(\mu_t - \eta\Omega) \simeq \rho_a(\mu_t)$ . In the limit  $|eV| \gg \Omega$  Eq. (31) becomes a linear function of applied voltage, in agreement with the result obtained by Gao  $et\ al.^{12}$  from a Boltzmann distribution among different vibrational levels.

As to a relation between  $R_{\rm in}$  and  $\Gamma_{\rm iet}$  in this limit, comparing Eqs. (23) and (29), we find that

$$|R_{\rm in}| - \Gamma_{\rm iet} = 2\left(\frac{\Delta_t}{\Delta_s}\right)^2 \gamma_{eh}^s \frac{(|eV| - \Omega)|eV|}{\Omega^2} \Theta(|eV| - \Omega).$$
(32)

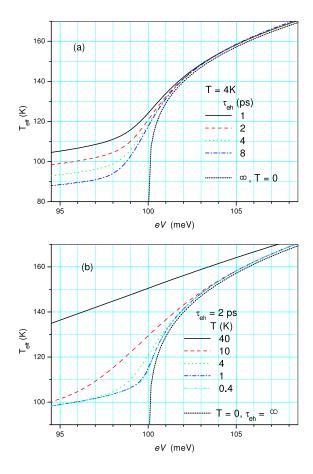


FIG. 3: Voltage dependences of the effective temperature, calculated for bath temperature T=4 K and different vibrational lifetimes (a); for  $\tau_{eh}=2$  ps and different temperatures (b). Short dotted line in both panels shows the effective temperature in the simple approximation neglecting the phonon broadening effect,  $\tau_{eh}=\infty$ , and at T=0,  $\Gamma_{\rm iet}(V)\propto |eV|-\Omega$ .

Because  $(\Delta_t/\Delta_s)^2 \ll 1$ ,  $|R_{\rm in}| \approx \Gamma_{iet}$ . The linear relation between  $\Gamma_{\rm iet}$  (or approximately  $R_{\rm in}$ ) and the bias voltage holds for  $eV \gg \Omega$ , which is a case of a Xe atom transfer between a Ni substrate and a STM tip ( $\Omega$ =4 meV and V=20-200 mV). 1,12

As to the adsorbate motion rate, in this limit a linear dependence of  $\Gamma_{\rm iet}(V)$  on  $|eV|-\Omega$  (Eq. (31)) and a condition of  $\gamma\gg\Gamma_{\rm iet}(V)$  yield the power-law dependence

$$R(V) \propto (|eV| - \Omega)^n$$
 (33)

for Eq. (16), in agreement with the analysis in Ref. 12. The opposite case  $\gamma \ll \Gamma_{\rm iet}(V)$  implies infinite effective temperature which is not consistent with an assumption of activation-type-law for a reaction rate Eq.(17).

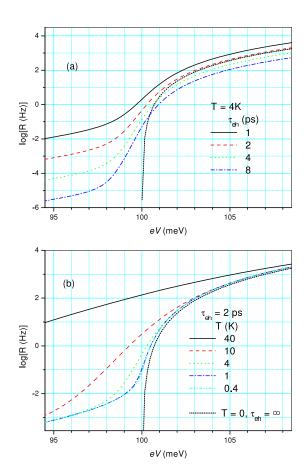


FIG. 4: Voltage dependences of the logarithm of the transfer rate, calculated for bath temperature T=4 K and different vibrational lifetimes (a); for  $\tau_{eh}=2$  ps and different temperatures (b). Short dotted line in both panels shows the transfer rate in the simple approximation neglecting the phonon broadening effect,  $\tau_{eh}=\infty$ , and at T=0,  $R(V) \propto (|eV|-\Omega)^n$ , n=3.

### C. Numerical examples

We are in a position to compare the relation between inelastic tunneling rate  $R_{in,e}$  and vibrational generation rate  $\Gamma_{\rm iet}$  as a function of V for several values of the vibrational relaxation time and temperature. Numerical calculations are performed for a set of parameters:  $\varepsilon_a$ =2 eV above the Fermi level of the substrate,  $\Delta_s$ = 1.0 eV,  $\Delta_t$ =0.025 eV,  $\Omega$ =100 meV, and different temperatures T=0.4,1,4, and 40 K. The electron-vibrational coupling constants were taken  $\chi=500,354,250$  and 177 meV, which at eV=0 and given  $\Delta_{s,t}$  correspond to vibrational linewidth  $\gamma_{eh}=0.66,0.33,0.16,$  and 0.08 meV (or vibrational lifetimes  $\tau_{eh}=\hbar/\gamma_{eh}=1,2,4,$  and 8 ps), respectively.

Figure 2 shows the calculated vibrational generation rates Eq. (21) (circles) and the corresponding inelastic currents Eq. (23) (lines) at fixed temperature for different vibrational lifetimes (panel a) and for fixed vibrational

lifetime for different temperatures (panel b). The generation rates are given in nA and also in  $\mu eV$  (left and right vertical axes in Fig. 2). Because the vibrational linewidths are taken in the range of 0.088 - 0.66 meV, it is clear that all the calculated rates are well within the condition  $\gamma \gg \Gamma_{\rm iet}(V)$ . It is seen that, in agreement with the analysis above, the inelastic current starts to exceed slightly the vibrational generation rate above the threshold of inelastic tunneling. As to the latter, it grows approximately linearly,  $\propto |eV| - \Omega$  above the threshold. The differences from the simple linear dependence arise near the threshold. Instead of abrupt switching on of the inelastic current and vibrational generation rate, there is a gradual growing of both. The physical reason is the temperature and lifetime broadening of the IET threshold. The temperature broadening has been analyzed previously (see, e.g., in Ref.23). The lifetime broadening was not analyzed, at least in part of its influence on the overheating and adsorbate motions. As we will see below, a different influence of temperature and lifetime broadenings allows, in principle, to separate these two mechanisms from the voltage dependence of the overheating and of motion rate below the IET threshold.

It becomes more evident from Fig. 3, where the calculated voltage dependencies of the effective temperature Eq. (15) for the same parameters as in Fig. 2 are displayed.

Note that above the IET threshold,  $|eV| \gg \Omega$  the overheating does not depend on the vibrational lifetime as well as on the temperature and approaches a universal linear dependence Eq. (31)  $\propto |eV| - \Omega$ . The reason for this is the cancellation of  $\chi^2$  in the nominator and denominator of  $\Gamma_{\rm iet}/\gamma_{eh}$ , if the e-h scattering Eq. (12) is the main channel of vibrational relaxation,  $\gamma \approx \gamma_{eh}$ . As a result, the stationary vibrational occupation number (30), effective temperature (15), and rate of adsorbate motion (16) do not depend on the adsorbate-vibration coupling constant. We have already mentioned this fact previously.<sup>17</sup> This effect takes place only above the IET threshold.

Whereas near and below the threshold,  $|eV| \lesssim \Omega$ , the effective temperature becomes lifetime and bath temperature dependent. First of all note that, in a seeming contradiction with a simple understanding that a shorter lifetime means better cooling, an opposite dependence is seen in Fig. 3a: the overheating grows with the lifetime decrease! The explanation is very simple: at low temperatures and below the IET threshold, the only reason of the nonzero inelastic current and overheating is the finite lifetime broadening. Which grows with the lifetime decrease. Mathematically, an additional power of  $\chi^2$  is brought into  $\Gamma_{\rm iet}$  below the IET threshold because of integration of  $\Gamma_{\rm in}(\omega) \propto \chi^2$  in Eq. (21) over the tail of the vibrational density of states at large detuning  $\gamma_{\rm ph}(\omega) \propto \gamma_{eh}/(\omega - \Omega)^2$ , which is  $\propto \chi^2$  too.

Figure 3b shows that, as anticipated, the temperature broadening is negligibly small in comparison with lifetime broadening, for lower temperatures  $k_BT \lesssim \gamma_{eh}$ .

For example, all  $T_{\rm eff}$  curves in Fig. 3b, calculated with  $\gamma_{eh}=0.33~{\rm meV}$ , merge into a single limiting curve starting from bath temperatures  $T<1~{\rm K}~(k_BT<0.9~{\rm meV})$ . This limiting curve corresponds to a T=0 solution for effective temperature with a finite vibrational lifetime.

Another interesting thing can be seen in Fig. 3b: the temperature broadening at higher temperatures,  $k_BT \gtrsim \gamma_{eh}$ , is localised within a finite range of several  $k_BT$  near the IET threshold, whereas the finite lifetime broadening is characterized by a long tail of strong overheating even at  $|eV| \ll \Omega$ . The explanation is that the latter is due to Lorenzian tail of the vibrational density of states, whereas the temperature broadening has a Gaussian tail.

Figure 4 plots R(V) Eq.(17) for the same set of parameters as before and barrier hight equal to n=3 vibrational excitation quanta. It shows that although with the increase of voltage above the IET threshold  $eV > \Omega$ , the rates of motion reach eventually the limiting power law dependence Eq.(33), in the vicinity of the threshold this dependence is different, depending on the relative values of  $k_BT$  and  $\gamma_{eh}$ . And below the threshold, at  $|eV| \ll \Omega - k_BT$ , the rate of motion is fully due to the vibrational lifetime broadening, thus making it to grow with the decrease of the vibrational lifetime.

# IV. CONCLUDING REMARKS

We have studied a formal relation between the inelastic tunneling current, vibrational generation rate and vibrational heating caused by the current-induced vibrational excitation of single adsorbates on metal surfaces. The nonequilibrium process of the electron tunneling between the tip and substrate through the adsorbate level is described by coupled Dyson and kinetic equations of the Keldysh-Green's functions. The inelastic tunneling current and the vibrational generation rate are obtained within the second-order perturbation with respect to the electron-vibration coupling based on the adsorbateinduced resonance model. We show that the vibrational generation rate slightly differs from the absolute value of the inelastic tunneling rate. The linear dependence of the vibrational generation rate on the bias voltage is valid for the extreme cases of  $|eV| \gg \Omega$  and the slowly varying adsorbate density of states over the applied voltage. Under these conditions the rate of adsorbate motions via the step-wise vibrational ladder climbing due to the inelastic tunneling current is characterized by a simple power-law dependence on the bias voltage or the tunneling current. It is found that the effects of bath temperature and vibrational damping manifest themselves in the vicinity and below the IET threshold, at  $|eV| \lesssim \Omega$ . The temperature broadening manifests itself only at relatively large bath temperatures,  $k_B T \gtrsim \gamma_{eh}$ . The important thing is that whereas the bath temperature broadening is confined to a narrow range of several  $k_BT$ , the vibrational lifetime broadening effect extends to a much larger interval of voltages below the IET threshold.

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